

# Chemistry

## Molecular Orbital Theory

motnotes.doc

Like valence bond theory discussed previously, molecular orbital theory is a method of mathematically describing the changes in orbitals that take place when bonds occur between atoms. However, unlike valence bond theory which only hybridizes those orbitals that directly take part in end-on ( $\sigma$ ) bonding, MOT blends all the orbitals in all the energy levels in the bonding atoms.

Molecular orbital theory is able to predict some of the observed behavior of molecules that valence bond theory fails to explain.

The discussion of MOT will be restricted to those elements of the 1<sup>st</sup> and 2<sup>nd</sup> period of the periodic table. The best way to understand MOT is to study the diagrams in the chapter and follow the examples but I will outline specific features of this theory that you should pay particular attention to.

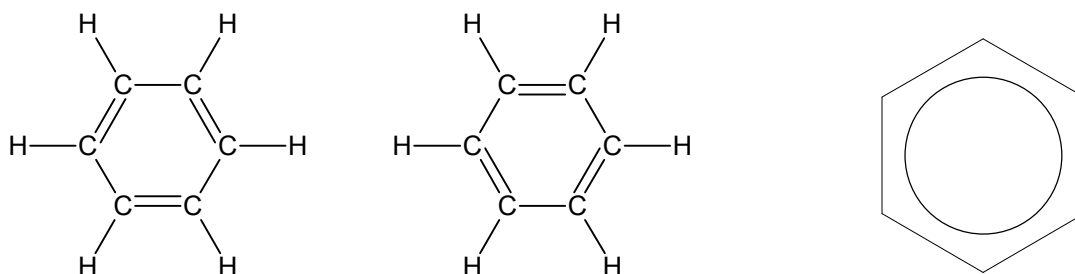
1. For each pair of combining atomic orbitals in the original atoms, a new pair of molecular orbitals form to replace them. One orbital (called the bonding molecular orbital) is lower in energy than the original atomic orbitals and contributes to the strength of the bond. The other (known as the antibonding molecular orbital) is higher in energy than the initial atomic orbitals and detracts from the strength of the bond.
2. Hund's rule, the Pauli exclusion principle and the Aufbau principle still apply when placing bonding electrons in molecular orbitals.
3. Antibonding orbitals are designated with an asterisk or "star" \*. For instance in the end-on overlap of the 1s orbitals of a diatomic hydrogen molecule, the bonding molecular orbital is designated  $\sigma_{1s}$  (sigma one-s) and the antibonding orbital is designated  $\sigma^*_{1s}$  (sigma one-s star).
4. In more complex molecules there can be a third type of bond, known as a nonbonding molecular orbital that neither contributes nor detracts from the strength of the bond. They will not be treated here.
5. The bond order determines the likelihood of a particular molecule and is given by
$$\text{Bond order} = \frac{(\text{number of [valence] } e^- \text{ in bonding MOs}) - (\text{number of [valence] } e^- \text{ in antibonding MOs})}{2}$$
6. A bond order of zero means that a particular molecule is unlikely. Positive bond orders are favorable.
7. Diatomic molecules containing the same elements are known as *homonuclear*.
8. For elements of the second period that bond using p orbitals, one set of sigma and two sets of pi bonding and antibonding orbitals are formed for a total of 6 orbitals. (Note again that the number of orbitals combined determines the number of molecular orbitals formed, since each bonding atom would be contributing 3 orbitals from their p-sublevel for a total of six orbitals).
9. The energy of the molecular orbitals change with the elements and the number of electrons change. Note that this can even impact the order in which the MO are filled (for instance, look at the difference between  $N_2$  and  $O_2$  on the chart in your textbook).
10. If you construct a MO diagram for  $O_2$ , you can see the observed paramagnetic properties of the molecule (i.e. 2 unpaired electrons in a  $\pi^*_{2p}$  MO) that valence bond theory failed to predict.

Try Exercise 10.10 on page 447. (Answer: 5/2 or 2.5)

## The Benzene Ring

Benzene is a cyclic organic molecule with very special properties. It is produced in vast amounts and is used as the starting material for many products.

Its ring structure was first proposed by F. August Kekulé in 1865. The structure consists of two resonance hybrid structures consisting of a six carbon ring with alternating single and double bonds.



Each carbon consists of a  $sp^2$  hybridization which accounts for its flat structure and  $120^\circ$  bond angles between the carbons. The 4<sup>th</sup> electron in the valence shell of each of the six carbons combine to form three  $\pi$  bonding MOs and three  $\pi$  antibonding MOs. Since the three  $\pi$  bonding MOs are lower in energy, the six electrons occupy only the bonding MO orbitals giving a bond order of  $(6-0)/2 = 3$ . When this is combined with the six sigma bonds of the bonds between the carbons you get an average bond order of  $(3+6)/6 = 1.5$ . This is consistent with the average bond length and bond energy of the molecule. This also makes benzene an extremely stable molecule.

Benzene and its related compounds make up a class of substances known as *aromatic compounds* (named after the fact that early isolated compounds of this type had pleasant aromas.)

All other types of organic molecules that don't fit into this category are known as aliphatic compounds.

When designating substituents (side-branches) on a benzene ring, use the terms ortho (o) for a 1,2 position, meta (m) for a 1,3 positioning and para (p) for a 1,4 positioning.

For instance, the molecule below is known as 1,4-dichlorobenzene or p-Dichlorobenzene.

